

Understanding the kinetic solvent effects on the 1,3-dipolar cycloaddition of benzonitrile N-oxide: a DFT study

Benchouk, W.; Mekelleche, S. M.; Silvi, B.; Aurell, M. J.; Domingo, L. R.

Abstract :

The kinetic solvent effects on the 1,3-dipolar cycloaddition (13DC) of benzonitrile N-oxide with cyclopentene [T. Rispens and J. B. F. N. Engberts, *J. Phys. Org. Chem.* 2005; 18, 908–917] have been studied using density functional theory (DFT) at the B3LYP/6-31G(d) level. Solvent effects were analyzed by means of the polarizable continuum model (PCM). The analysis of the potential energy surface shows that this reaction follows an asynchronous concerted mechanism. The topological analysis of the electron localization function (ELF) of the turning points along the reaction pathway explains the diradical nature of mechanism of this reaction. Inclusion of solvent effects does not substantially modify this behavior. The present study points out that, contrary to Diels–Alder reactions, the increase in the solvent polarity leads to a slow inhibition of the 13DC reaction, because of the low polarity of the transition state. Explicit solvation involving the coordination of one water molecule to the dipole puts in evidence the importance of hydrogen bonding in the modest acceleration of this 13DC reaction. These results are in good agreement with experimental outcomes.

Keywords : 1,3-dipolar cycloaddition; benzonitrile N-oxide; density functional theory; solvent effects; electron localization function.

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